A Study of Lubricants on Silver Flakes for Microelectronics Conductive Adhesives

Daoqiang Lu, *Member, IEEE,* Quinn K. Tong, and C. P. Wong, *Fellow, IEEE*

***Abstract*— Conductive adhesives are composites of polymer matrixes and metal fillers (conductive elements). Silver (Ag) flakes are widely used as fillers for electrically conductive adhesives (ECA's). Generally, there is a thin layer of organic lubricant coated on the commercial Ag flake surface. This lubricant layer is needed for eliminating the Ag particle agglomeration while dispersing the Ag filler into the polymeric resin. Therefore the lubricant influences rheology, conductivity, and other properties of ECA's. The nature of the lubricant on a Ag flake and the interaction between the lubricant and the Ag flake surface were studied by diffuse reflectance infrared spectroscopy (DRIR). Thermal decomposition of the lubricant was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition, the effects of some chemical compounds on lubricant removal and the enhancement of conductivity of the ECA were also investigated. It was found that**

1) **a chemical bonding was formed on the Ag flake surface between the lubricant and Ag;**
2) **the short chain acids replaced the long chain lubricants;**
3) **an ether and a poly(ethylene glycol) enhanced electrical conductivity by partially removing the Ag flake lubricants.**

***Index Terms*—Conductive adhesives, interaction, lubricant removal, lubricants, silver flakes.**

I. Introduction

CONDUCTIVE Adhesive technology is an attractive technology which involves fewer process steps and lower cure temperatures than soldering while avoiding the environmental issues surrounding chlorofluorocarbon (CFC)-based flux cleaners and the use of lead [1]–[8]. Electrically conductive adhesives (ECA's) are composites of polymer matrixes and metal fillers. Among metal fillers, Ag flakes are most widely used because they are highly electrically conductive and, unlike many other metals, their oxides are also conductive.

Generally, Ag flakes are produced from Ag powders by mechanical milling [9]. Organic lubricants are added during milling and a thin layer of lubricant remains on the surface of Ag flakes after production. This organic layer plays an important role for the performance of ECA's, including the dispersion of the Ag flakes in the adhesives, rheology of the adhesive formulations, and electrical conductivity of the ECA after cure. This layer of lubricant is nonconductive, and as such, it is believed that an ECA becomes conductive only after this layer had been removed [10].

The chemical nature of a fatty acid lubricant on a Ag flake, the interaction between the lubricant and the Ag flake surface, the thermal decomposition of the lubricants, and the effects of certain chemicals on lubricant removal and the enhancement of electrical conductivity of ECA's are discussed in this paper.

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II. Experimental

A. Materials and Sample Preparation

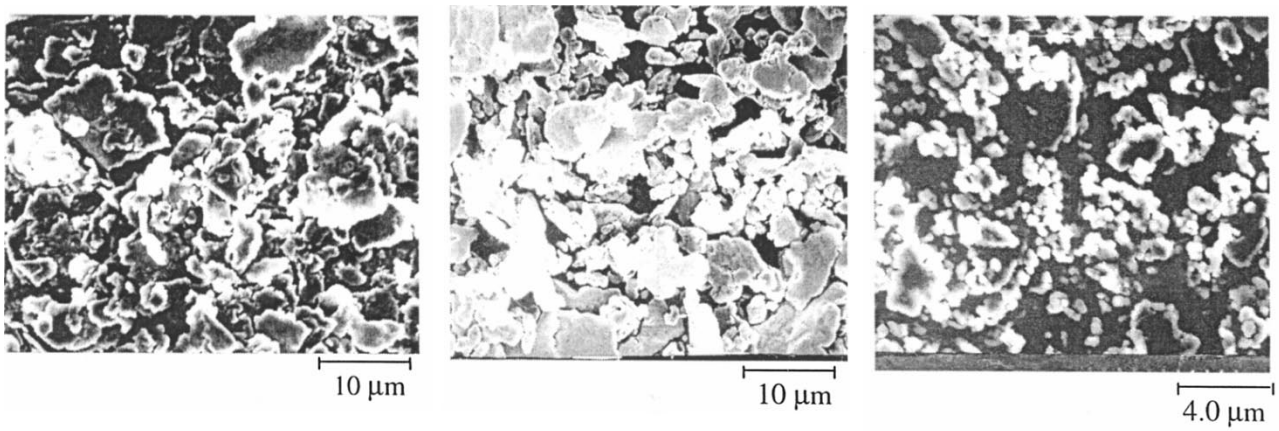
All the Ag flakes used in this study are commercial samples. Acetic acid, adipic acid, diethylene glycol butyl ether, poly(ethylene glycol), methanol, tetrahydrofuran (THF), and acetone were purchased from Aldrich Chemical Company and used without further purification.

The adhesive formulations were prepared by mixing appropriate amount of Ag flakes with the base resin (epoxy and hardener). The filler loading of the adhesives was 80% by weight. The epoxy resin (RSL 1738) used here was purchased from Shell Chemical Co. and the hardener, 2E4MZ-CN, was purchased from Shikoku Chemicals Corporation. All materials were used as received.

Resistivity of an ECA was calculated from the bulk resistance of the ECA specimen with specific dimensions. Two strips of an adhesive tape were applied onto a pre-cleaned glass slide with a gap of 0.1 in (0.254 cm) between these two strips. The thickness of the strips was used to define the ECA thickness. The conductive adhesive paste was then spread within space by means of a doctor blade, and then the tapes were removed. After cure, the bulk resistance of this ECA strip was measured. Thus, the length of the specimen is length of the glass slide (75.60 cm); its thickness is that of the adhesive tape (0.007 cm); and its width is that of the gap between the two adhesive strips (0.254 cm).

B. Instrumentation

A Perkin–Elmer DSC-7 was used in this study to detect and characterize the organic lubricants on the Ag flakes. A 10 °C/min heating rate was selected. Sample size for DSC studies was about 20 mg. Weight loss of the Ag flakes during heating was studied with the thermogravimetic analyzer, TGA model 2050, from TA Instruments. A 10 °C/min heating rate was used. Sample size in TGA studies was about 60 mg. The diffuse reflectance infrared spectra were collected with



(a) (b) (c)

Fig. 1. Scanning electron micrographs of three types of Ag flakes.

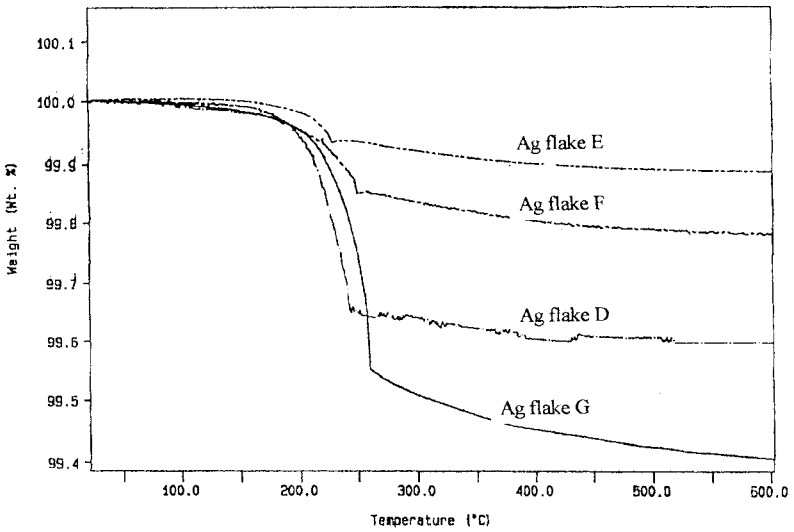


Fig. 2. Weight loss of Ag flakes (in air).

the Nicolet FTIR model 205. The particle size and shape of the Ag flakes were investigated with the Hitachi S-800 scanning electron microscope (SEM). Rheology study of the adhesive formulations was conducted with the Rheometer, model AR1000-N, from TA Instruments. A 4 cm steel parallel plate fixture was used in the study. All measurements were conducted at room temperature. A Keithley 2000 multimeter with a four-point probe was used to measure the bulk resistance of ECA samples.

III. Results and Discussion

A. SEM Studies

In order to find out what kinds of Ag fillers are used in commercial conductive adhesives, three commercial conductive adhesives, all of which are epoxy based adhesives, were washed with acetone for four times to remove resin parts. Then the Ag fillers were dried at room temperature and under vacuum. SEM pictures of these three recovered Ag fillers, Ag fillers A, B, and C, are shown in Fig. 1(a)–(c). Fig. 1(a) shows that Ag filler A contains flakes with size range of 2–14 μm diameters. Fig. 1(b) indicates that Ag filler B contains three kinds of particles in the mixture: 3–15 μm diameter flakes, small irregular fillers, and very small sphere fillers. Fig. 1(c) shows that Ag filler C contains much smaller particles and it is a mixture of flakes and spherical fillers.

B. Thermal Studies

DSC and TGA are convenient and reliable techniques to characterize the lubricants on Ag flakes. These techniques can be used to detect the existence of the trace amount of organic lubricants on Ag flakes. Four commercial Ag flakes, Ag flakes D, E, F, and G were studied by TGA. All of the four Ag flakes have lubricants on their surfaces based on information from their manufacturers. The weight loss results of these Ag flakes are shown in Fig. 2. Weight loss during heating indicates the existence of lubricants on the Ag flakes. All the Ag flakes showed significant weight loss at the temperature range from 200–300 °C, however the weight loss percentages of these samples are different.

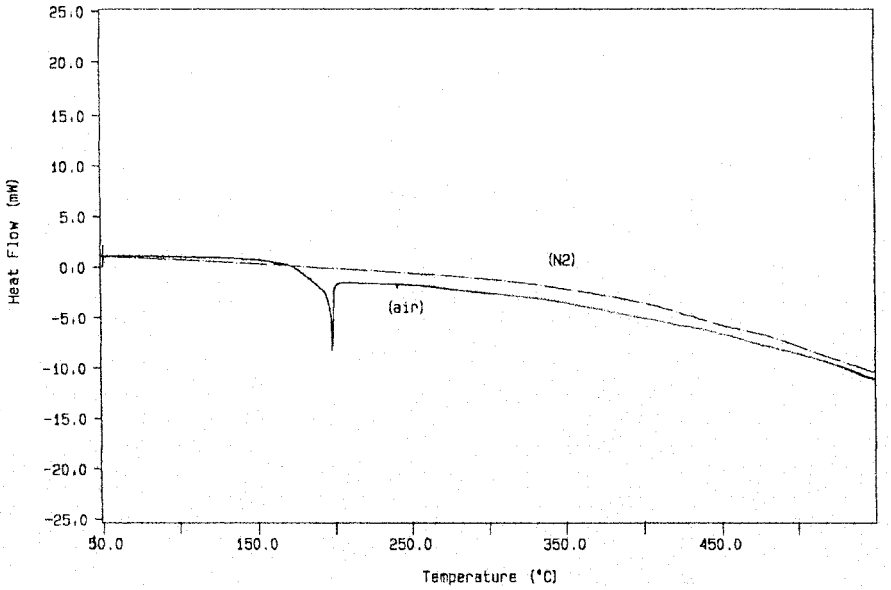


Fig. 3. DSC curves of Ag flake E in air and N_2.

TABLE I
DSC EXOTHERMIC PEAKS OF THE Ag FLAKES

Ag flake	Lubricant	Peak temperature (°C)
D	Stearic acid	248
E	Isostearic acid	199
F	Oleic acid	235

All of the four Ag flakes were then studied by DSC in two different atmospheres: air and nitrogen (N_2). The results of all the Ag flakes were similar. Therefore, the results of only one of the Ag flakes, Ag flake E, were shown in Fig. 3. An exothermic peak was detected in the DSC curve when the sample was run in air. But this exothermic peak was absent when the sample was run in N2 atmosphere. The exothermic peak is a clear indication of the presence of the lubricants. Absence of the exothermic peak in N_2 suggests that the exothermic peak is related to an oxidation process of the lubricants.

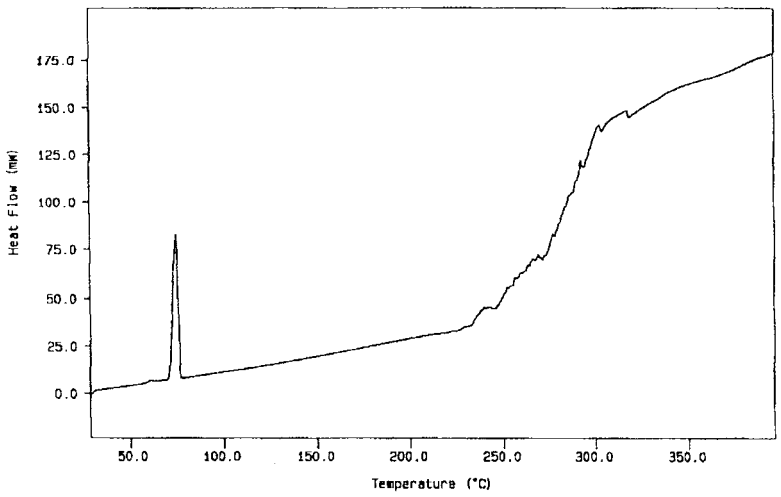
DSC was used here to characterize the organic lubricants on the Ag flakes. According to the information requested from the manufacturers, three of the Ag flakes (Ag flakes D, E, and F) have different lubricants. Lubricant information of the other Ag flake (Ag flake G) was not available because its manufacturer was not willing to release it. Therefore, Ag flake G was not included here. DSC results (in air) were given in Table I. As can be seen from Table I, Ag flakes with different lubricants showed exothermic peaks (in air) in the DSC curves at different temperatures ranging from 199–248 °C. From the DSC and TGA results, we can see that these Ag flakes showed significant weight losses and exothermic peaks at the same temperature ranges, which suggests that there might be a correlation between the weight loss and exothermic peak for each Ag flake.

In order to elucidate what is responsible for the DSC exothermic peak, we conducted another study. A blank neat Ag powder was lubricated by stearic acid which is a common lubricant for Ag flakes. Then the blank neat Ag powder, the lubricated Ag powder, and stearic acid were studied by DSC in an air atmosphere. These DSC curves are given in Fig. 4 (a)–(b). It was found that there were no exothermic peaks in the DSC curves of the blank Ag (neat) powder and stearic acid but an exothermic appeared after the blank Ag (neat) powder was lubricated by stearic acid. This result indicates that there is a chemical interaction (or bonding) between the lubricant and the Ag powder and the exothermic peak is the demonstration for this interaction. However, the new exothermic peak of the lubricated Ag powder appeared at a slightly higher temperature than does that of the Ag flake D whose lubricant was also stearic acid. The reasons were not clear yet. The Ag flake D was lubricated by the manufacturer. The lubrication process might be different from ours. Different lubrication processes might slightly influence the interaction between the lubricant and the Ag surface. Another possible reason may be due to a measurement error.

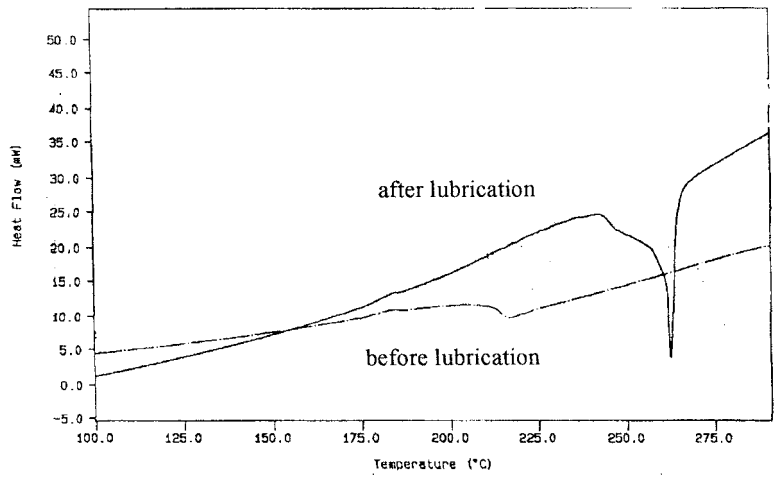
C. DRIR Studies

Thermal studies suggest that there is a certain kind of bonding formed between the Ag flake surface and the lubricants. DRIR is a reliable technique to characterize the chemical structures of the trace amount of organic lubricants on the Ag flake surface.

All of the four Ag flakes were studied by using DRIR. They all showed very similar DRIR spectra because their lubricants had similar chemical structures. The spectrum of one of the Ag flakes, Ag flake E, was shown in Fig. 4. The lubricant on this Ag flake is isostearic acid according to the manufacturer. The absorption peaks near 2800–2900 cm^{-1} correspond to the C-H stretching in the long carbon and hydrogen chain



(a)



(b)

Fig. 4. (a) DSC curve of stearic acid (in air). (b) DSC curves of the blank Ag powder before and after lubrication (in air).

of the lubricant. The peak at ca. 1670 cm^{-1} is due to C = O stretching in the carboxylic acid group of a free acid and its absorption intensity is usually very strong. However, as can be seen from Fig. 4, this peak is very weak in this case. The weak absorption indicates that there is only a very small amount of free acid on the Ag flake surface. The strong peaks at ca. 1570 and 1400 cm^{-1} which are not present in the spectrum of the free acid correspond to asymmetric and symmetric stretching of carboxylate anion ($-COO^{-}$), respectively [11], 12]. The aforementioned DRIR results confirmed the fatty acid nature of the lubricant. Also the results indicate that most of the fatty acid on the Ag flake surface forms a salt with the Ag flake surface and only a small portion of the lubricant is in the form of free acid.

D. Effects of Some Chemicals on Lubricant Removal or Replacement

The chemicals employed here include some solvents (methanol, acetone, and tetrahydrofuran), short chain acids (acetic acid and adipic acid), an ether (diethylene glycol butyl ether), and a poly(ethylene glycol). Ag flake E was treated with these chemicals. The treatment procedure is as follows:

1) Ag flake was mixed with the chemicals or its solution (if it is a solid, e.g., adipic acid);
2) mixture was kept at room temperature overnight;
3) Ag flake and the chemicals were separated by centrifuging;
4) Ag flake was washed three times with a solvent, usually methanol;
5) after drying, the treated Ag flake was studied by DSC and DRIR.

As mentioned in the previous sections, the exothermic DSC peak of the Ag flake is probably due to the oxidation of the lubricant. It was believed that the exothermic peak is due to the oxidation of the long carbon-hydrogen chain residue which was formed after the decarboxylation of the fatty acid lubricant [10]. Therefore, the peak area (enthalpy, ΔH, J/g) should be directly proportional to the amount of lubricant on the Ag flake surface and the peak area can be used to estimate semi-quantitatively the relative amount of the organic lubricants

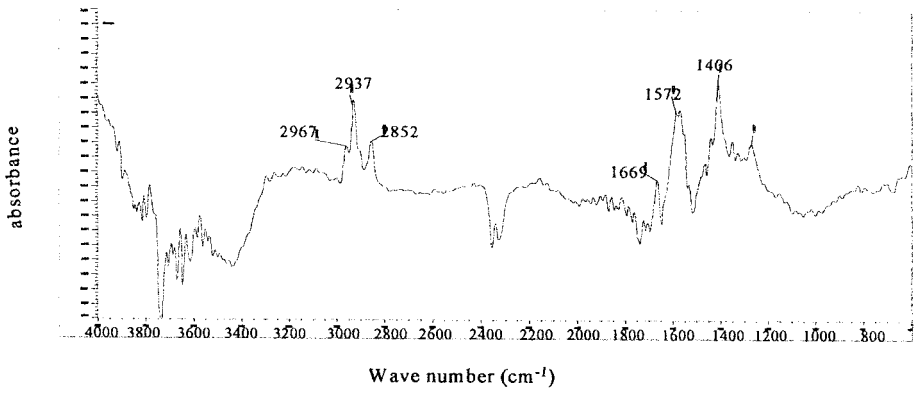


Fig. 5. DR-IR spectrum of Ag flake E.

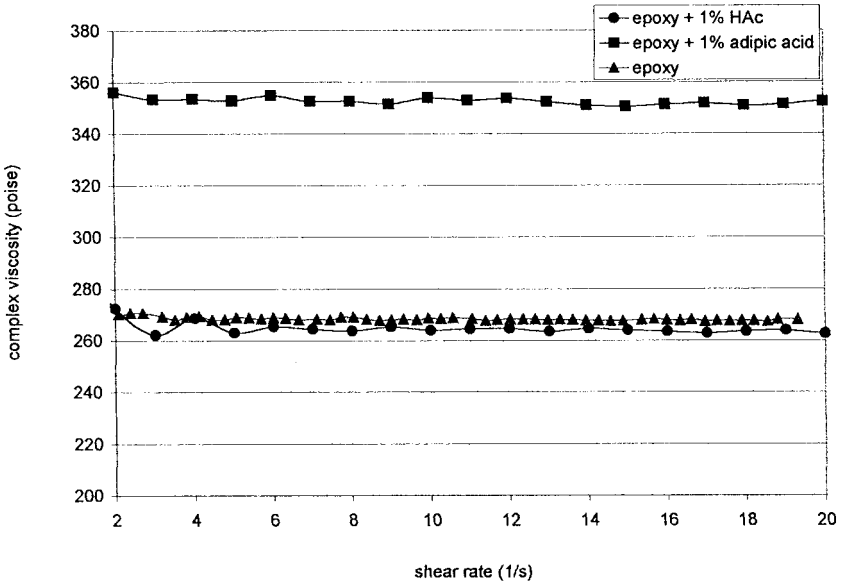


Fig. 6. Effects of HAc and Adipic acid on viscosity of the epoxy resin.

present on the Ag flake surface. As for DRIR spectra of the samples, there should be no significant spectral changes after treatment if the chemical has no effect on the lubricant removal.

1) Some Common Solvents: Three widely used solvents, methanol, tetrahydrofuran, and acetone, were selected. After treatment with these solvents, the Ag flake was studied by DSC and DRIR. No DSC and DRIR difference were observed for the untreated and treated Ag flakes. Therefore, these solvents didn't have significant effect on the lubricant removal. The fact that the lubricant could not be washed off by the solvents indicates that there is strong bonding between the lubricant and the Ag flake surface which is consistent with DSC and DRIR results in the previous sections.

2) Short Chain Acids: Two short chain acids, acetic acid (HAc) and adipic acid, were used in this study. First, the effects of the acids on an epoxy-based ECA formulation and its epoxy resin were investigated. This conductive adhesive was also filled with the Ag flake E. Viscosity changes of the epoxy resin and the ECA formulation after addition of a small amount (1% wt.) of acids were shown Figs. 6 and 7, respectively. As can be seen from Fig. 6, HAc slightly decreased the viscosity of the epoxy resin. However, adipic acid increased the viscosity of the epoxy resin a little because it was a solid. Therefore, the acids did not react with epoxy and changed its viscosity. However, from Fig. 7, we can see that viscosities of this ECA formulation increased dramatically after addition of a small amount of acids. The result suggests that these acids strongly affected the interaction between the Ag flake and the resin and the interaction among Ag flakes.

Then the Ag flake (Ag flake E) of the above ECA formulation was treated with HAc and adipic acid methanol solution. From DSC studies, it was found that there are dramatic ΔH changes, 15 J/g for untreated Ag flake, 3 J/g for HAc-treated Ag flake, and 2 J/g for adipic acid-treated Ag flake. Either of the two processes, lubricant removal or lubricant replacement by the acids, might have happened here. If the lubricant was removed by the acids, then ΔH will decrease. If the lubricant was replaced by the short chain acids, the ΔH also will decrease because oxidation of the short carbon-hydrogen chains of adipic acid or acetic acid will generate much less heat.

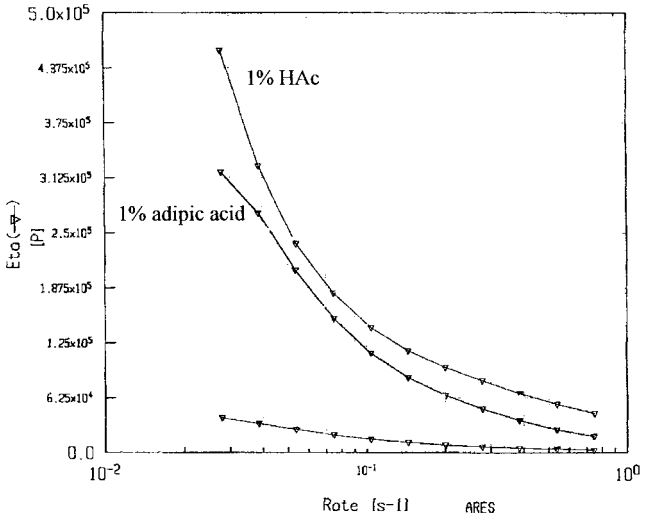


Fig. 7. Effects of HAc and Adipic acid on viscosity of an ECA.

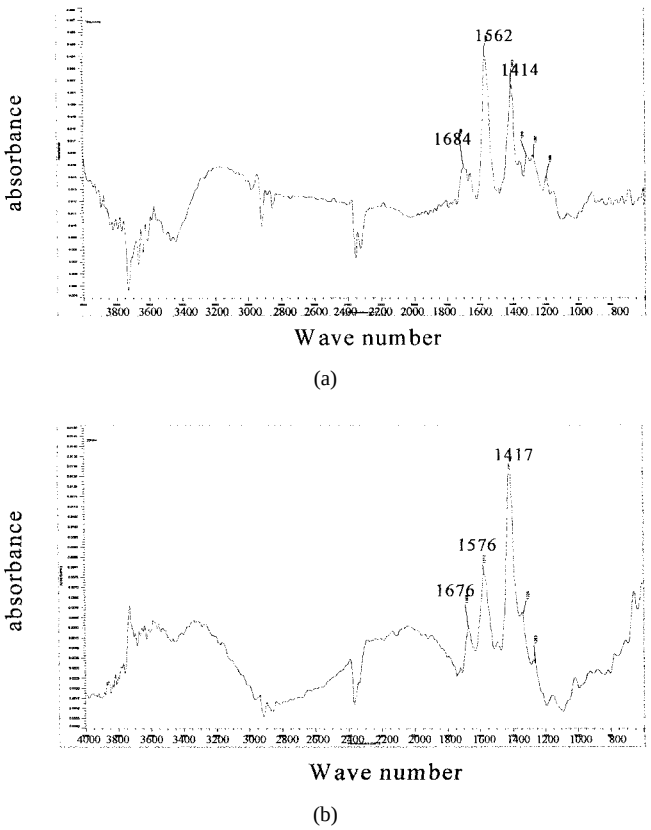


Fig. 8. DRIR spectra of HAc treated (a) and Adipic acid treated Ag flake E (b).

The DRIR spectra of the HAc-treated and adipic acid-treated Ag flakes are shown in Fig. 8 (a) and (b), respectively. Compared to the spectrum in Fig. 5, the peaks at ca. 2800–2900 cm^{-1}, which correspond to C-H stretching, disappeared after the acid treatments but other peaks remained. Compared with C-H stretching intensity of the fatty acid, the C-H stretching intensity of adipic acid and HAc is very low. However, the C = O and COO^- stretching intensities of adipic acid and HAc are similar to those of the fatty acid

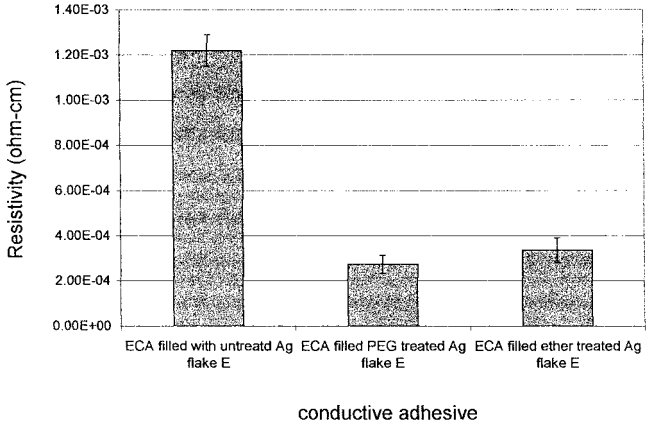


Fig. 9. Resistivity of three ECA's filled with untreated and treated Ag flake E.

lubricant. If the lubricant was partially removed by the acids, then the intensities of all the peaks should decrease. However, if the lubricant was replaced by the acids, the C-H stretching intensity will decrease dramatically but the intensities of other peaks should not change much. It seems that above DRIR results can be better explained by lubricant replacement other than lubricant removal.

3) Effect of an Ether and a Poly(ethylene glycol): An ether, diethylene glycol butyl ether (DGBE), and a poly(ethylene glycol) (PEG) with low molecular weight (ca. 200) were used as conductivity promoters [1], [13]. Addition of a small amount of DGBE and PEG to a Ag flake-filled ECA formulation can improve electrical conductivity significantly. However, the reasons for these chemicals' conductivity improvement are still unclear at present.

Effect of these two chemicals on electrical conductivity was confirmed first. An epoxy based ECA formulation which was filled with the Ag flake E was employed in this study. The resistivity of the ECA decreased significantly after addition of a small amount (two parts per hundred resin) of DGBE or PEG, from 1.4×10^{-2} Ω-cm for the original ECA sample (without DGBE or PEG), to 3.4×10^{-3} Ω-cm for the ECA sample with the DGBE, and 3.7×10^{-3} Ω-cm for the ECA with PEG.

The Ag flake of above ECA formulation, the Ag flake E, was treated with the ether and the polyethylene glycol. Then the treated Ag flakes were studied by DSC and DRIR. It was found that DSC peak area changed from 15 J/g (Ag flake E) to 8 J/g (ether treated Ag flake E) and 4 J/g (PEG treated Ag flake E), respectively. However, treated Ag flakes showed the same DRIR spectra as the untreated Ag flake. The results suggest that the lubricant was partially removed rather than replaced by the ether and PEG after treatment. Therefore, it is believed that the ether and PEG improved conductivity by partially removing the lubricant on the Ag flakes. Another experiment was conducted to confirm this idea. Three ECA formulations which had the same resin formulation were filled with untreated Ag flake E, the ether treated Ag flake E, and the PEG treated Ag flake E, respectively. These three ECA's had the same filler loading, 80% wt. After they were cured under the same condition, bulk resistance was measured. The

bulk resistivity results are given in Fig. 9. As can be seen in this figure, both ECA's filled ether treated and PEG treated Ag flake E had lower resistivity than the ECA filled with untreated Ag flake E. This study proved that the ether and the PEG improved conductivity by partially removing the Ag flake lubricant.

IV. Conclusion

DSC studies indicated that

1) Ag flakes with different lubricants showed the DSC exothermic peaks at different temperatures;
2) there is a chemical interaction (bonding) between the lubricant and Ag flake surface;
3) the exothermic DSC peak is related to this lubricant-silver flake interaction;
4) the exothermic DSC peak probably is due to lubricant removal at high temperatures.

For the four commercial Ag flakes, they all showed significant weight loss at the temperature range from 200 °C to 300 °C but their weight loss percentages are different.

DRIR results of the Ag flake indicated that most of the fatty acid on the Ag flake surface formed salt with Ag surface and only a small part of the fatty acid is in the form of free acid.

Three common solvents (methanol, THF, and acetone) don't have obvious effect on Ag flake lubricant removal. However, short chain acids such as HAc and adipic acid can partially replace the lubricant of Ag flakes. Finally, diethylene glycol butyl ether and the PEG appeared to improve electrical conductivity by partially removing the nonconductive lubricant from the Ag flake surface.

References

[1] A. O. Ogunjimi, O. Boyle, D. C. Whalley, and D. J. Williams, "A review of the impact of conductive adhesive technology on interconnection," *J. Electron. Manufact.*, vol. 2, p. 109, 1992.
[2] C. P. Wong, D. Lu, S. Vona, and Q. Tong, "Fundamental understanding of electrically conductive adhesives," in *Proc. 1st IEEE Int. Polymeric Electron. Packag. Conf.*, 1997, p. 80.
[3] R. Pound, "Conductive epoxy is tested for SMT solder replacement," *Adhesive Age*, vol. 25, p. 86, 1985.
[4] H. L. Hvims, "Solder replacement," in *Proc. IEEE/CHMT Int. Electron. Manufact. Technol. Symp.*, 1993, vol. 15, p. 128.
[5] Y. C. Lee and P. M. Williams, " Solderless connection technology," *Manufact. Aspects Electron. Packag.*, vol. 65, p. 71, 1993.
[6] J. C. Jagt, P. J. M. Beris, and G. F. C. M. Lijten, "Electrically conductive adhesives: A prospective alternative for SMD soldering?," *IEEE Trans. Comp., Packag., Manufact. Technol. B*, vol. 18, no. 2, p. 292, May 1995.
[7] P. G. Harris, " Conductive adhesives: A critical review of progress to date," *Solder. Surface Mount Technol.*, 1995, p. 4.
[8] M. Zwolinski and J. Hickman, " Electrically conductive adhesives for surface mount solder replacement," *IEEE Trans. Comp., Packag. Manufact. Technol. C*, vol. 19, no. 4, p. 241, Oct. 1996.
[9] E. M. Jost and K. McNeilly, "Silver flake production and optimization for use in conductive polymers," in *Proc. ISHM'87*, 1987, p. 548.
[10] A. J. Lovinger, "Development of electrical conduction in silver-filled epoxy adhesives," *J. Adhesion*, vol. 10, p. 1, 1979.
[11] R. M. Silvertein and G. Clayton, *Spectrometric Identification of Organic Compounds*, 5th Ed. New York: Wiley, 1991, p. 118.
[12] L. K. Chau and M. D. Porter, "Fluorinated monomolecular assemblies: Model systems to probe chemical interactions at the polymer-metal interface," in *Proc. Mater. Res. Soc. Symp.*, 1988, vol. 154, p. 310.
[13] A. J. Lovinger, "Conductive adhesive system including a conductivity enhancer," U.S. Patent 4 356 505, 1982.

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